博 士 論 文 内 容 の 要 旨

専攻名 物質工学 専攻

講座名 分子工学 講座

氏 名 李 文 文

１ 論文題目（英文の場合は，和訳を付記すること）

Mechanism of Electrocatalytic Reduction of Dioxygen with Hemin
(ヘミンによる酸素の電気化学的触媒還元反応の機構)

２ 要 旨（和文 2,000 字程度又は英文 800 語程度にまとめること。）

The thesis deals with electrochemical reduction of dioxygen with hemin on different kinds of electrodes in different kinds of solutions in order to find functionality of hemin catalysis for dixoygen and its catalytic mechanism. The aim of this research is to investigate the mechanism of reaction, build the reaction model and discuss its application in normal which is based on analysis of the electrochemical reduction currents of dioxygen by hemin with different states on electrode surface in different kinds of solutions. This study was performed to improve understanding of the kinetic mechanism in heterogeneous catalysts for oxygen reduction reaction(ORR).

Chapter 3 is devoted to examining irreversibility of catalytic reduction of dioxygen by dissolved hemin. According to cyclic voltammogram(CV), peak currents in deaerated hemin solution is diffusion controlled, whereas that in aerated solution is represented as a sum of the diffusion current and a surface wave. The results mean that the catalytic current presents and it is caused by hemin incorporated with dioxygen. The calculated value of adsorption density is close to accepted values of

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the monolayer adsorption as well as reported values of adsorbed hemin. The agreement indicates that the catalytic reduction of dioxygen should occur at glassy carbon electrode surface by hemin in adsorbed species state in dimethyl sulfoxide (DMSO). The voltammograms figures showed that the catalytic current cannot keep a steady state even if dioxygen is supplied to the electrode by diffusion or convention. Actually the reaction will be interrupted if the adsorbed species is not dissolved at the oxidation at 0.3 V. In other words the electrode surface is not renewed sufficiently for the catalytic reaction. In order to keep the catalysis for a long time, it is necessary to remove the adsorbed species. Consequently, the catalysis is not suitable for an alternative to precious metals in fuel cells.

Chapter 4 is devoted to relationship between electrochemical catalysis and the generation of a dioxygen adduct of hemin. Two different conditions were performed to study the inner link of currents from hemin-coated electrode and dissolved hemin. At the hemin-coated electrode is not proportional to the amount of adsorbed hemin but is controlled by dioxygen because the hemin film is superfluous for dioxygen relatively on electrode surface. The catalytic current is controlled by diffusion of dioxygen, associated with the successive two-electron transfer reaction. The hemin-coated electrode can be used quantitative determination of dioxygen without rigorous control of the amount of hemin; In solution with dissolved hemin, the dioxygen adduct of hemin plays a role of an intermediate of the catalytic reaction, via the reaction equation: $O_2 + 2\text{hem}(Fe^{2+}) \leftrightarrow (\text{hem}(Fe^{2+}))_2O_2 \rightarrow O_2^{2-} + 2\text{hem}(Fe^{3+})$. Ultraviolet spectrum results supply a lateral confirmation of this reaction.